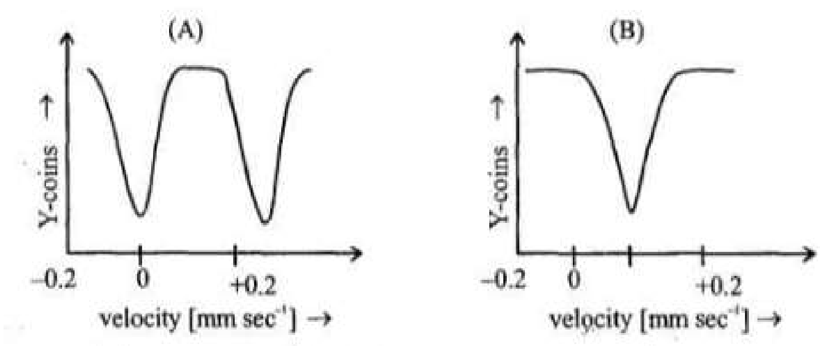
DPP- (1) Mossbauer

1. It Mössbauer spectrum of $Fe(CO)_5$ is recorded in the presence of a magnetic field, the original spectrum with two lines changes into the one with

(a) Three lines (b) Fout lines

(c) Five lines (d) Six lines

2. The Mössbauer spectra of two iron complexes are shown below. They may arise from (i) high-spin iron (III), (ii) high-spin iron (II) (iii) low-spin iron (III)



The correct mathches of spectra (A) and (B) with the complexes are

(a) A with (i) and (B) with (ii) (b) A with (ii) and B with (i)

(c) A with (iii) and (B) with (d) A with (ii) and B with (iii)

3. Mössbauer spectrum of complex [FeCl, 10–phenanthradine]$_2$ $(NCS)_2$] shows two lines at 300, four lines at 186 K, and again two lines at 77K. This can be attributed to

(a) Change in the co-ordination mode of NCS

(b) Change in the spin-state of iron

(c) Cis-trans isomerism

(d) Change in metal-ligand bond distances

4. The mössbauer spectra of $K_4[Fe(CN)_6]$ and $k_3[Fe(CN)_5No]$ consist of, ... line.

5. The Mössbauer spectra of $k_3[Fe(CN)_5No]$ consist of .... lines.

6. The Increasing order of isomer shift of the low spin complexes of

$[Fe(II)(CN)_5L]n^-$ (where L = NO^+, CO, CN, PPh_3, NO_2^-) is

(a) $NO^+ < PPh_3 < CO < NO_2^-$ (b) $NO_2^- < PPh_3 < NO^+ < CO$

(c) $NO^+ < CO < PPh^3 < NH_3$ (d) $NO^+ < CO < PPh_3 < NO_2^-$

Address : 50 Mall Road, Near GTB Nagar Metro Station Gate No 3, Kingsway Camp, Delhi 110009

Contact Us : 9990382567, 7082062392, 9717373074, 8285815185

7. In high spin complexes of Fe(II) and Fe(III), the isomer shifts values are :

(a) Fe(II) > Fe(III) both are positive
(b) Fe(III) > Fe (II) both are negative
(c) Both are almost equal and negative
(d) Both are almost equal and positive

8. Among the following which is having least isomer shift values?

(a) SnF_4 (b) $SnCl_4$ (c) $SnBr_4$ (d) SnI_4

9. The electrons which contribute to isomer shift in M.B. spectroscopy are :

(a) s-electrons (b) p-electrons (c) d-electrons (d) f-electrons

10. The number of lines in the mössbauer spectra and magnetic behaviour of deoxyhemerythrin.

(a) Single line and paramagnetic
(b) One doublet and diamagnetic
(c) One doublet
(d) One doublet and paramagnetic

11. The number of lines in the Mössbauer spectra and magnetic behaviour of oxyhemerythrin.

(a) Double line and paramagnetic
(b) Two doublet and paramagnetic
(c) Two doublet and diamagnetic
(d) None of these

12. The correct order of the isomeric shift in ^{119}Sn Mössbauer spectra of Sn Compound is

(a) Sn(covalent) > Sn^{2+} > Sn^{4+}
(b) Sn (covalent) > Sn^{4+} > Sn^{2+}
(c) Sn^{2+} > Sn (covalent) > Sn^{4+}
(d) Sbn^{4+} > Sn^{2+} > Sn (covalent)

13. The complexes ;

A : $[Fe(CN)_5NO]^{2-}$, B : $[Fe(CN)_5NH_3]^{2-}$, C : $[Fe(CN)_5CO]^{2-}$, D: $[Fe(CN)_5PPh_3]^{2-}$

Show a quadrupole split double line Mössbauer spectra.

The increasing order of $\Delta\theta_Q$ parameter values in the spectra is.

(a) $NO^+ < PPh_3 < CO < NH_3$
(b) $NH_3 < PPh_3 < CO < NO^+$
(c) $NO^+ < CO < PPh_3 < NH_3$
(d) $NH_3 < PPh_3 < NO^+ < CO$

14. In the spin complexes of Fe(II) and Fe(III), the isomer shifts values are

(a) Fe(II) > Fe(III) both are positive
(b) Fe(III) > Fe(II) both are negative
(c) Both are almost equal and negative
(d) Both are almost equal and positive

15. A particular Mössbauer nucleus has spins of 5/2 and 3/2 in its excited and ground states respectively. The number of lines obtained in its r-rays spectrum under the conditions.

A : Internal electric field gradient

B : no electrical field gradient but internal magnetic field are

(a) 1, 5 (b) 5, 12 (c) 5, 6 (d) 12, 6

16. Mösssbauer spectroscopy is concerned with

(a) Doppler effect
(b) Photoelectric effect
(c) Recoil effect
(d) Cotton effect

17. Electric qudrupolar splitting is dependent on

(a) Quadrupole moment of nuclei
(b) Electronic symmetry around the nucleus
(c) Ligand symmetry around the nucleus
(d) None of these

18. Which of the following are the pauameters of M.B spectroscopy?

(a) Number of signal
(b) Multiplicity of signal
(c) Positions of signal
(d) spilitting constant

ANSWER KEY

1.	(d)	2.	(b)	3.	(a,b)	4.	(1)	5.	(2)	6.	(c)	7.	(a)
8.	(a)	9.	(a)	10.	(d)	11.	(c)	12.	(c)	13.	(b)	14.	(c)
15.	(b)	16.	(a,c)	17.	(a,b,c)	18.	(a)						

HINTS & SOLUTION

2.Sol. (i) $Fe^{III} \rightarrow$ High spin – d^5 – spherical electronic configuration

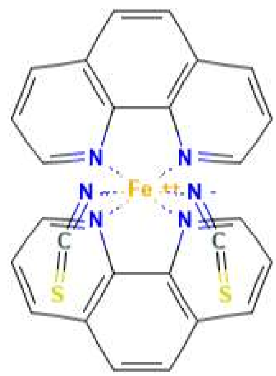
$t2g^3eg^2 \rightarrow$ No quadrupole spiltting singlet signal as shown in (B)

(ii) $Fe^{II} \rightarrow$ High spin – d^6 – Axial electronic configuration

$t2g^4eg^2 \rightarrow$ Quadrupole splitting, gives doublet signal as shown in (A)

(iii) $Fe^{III} \rightarrow$ Low spin – $t2g^5\ eg^\circ \rightarrow$ Axial electronic configuration quadrupole spitting, doublet signal as shown in (A)

3.Sol. [Fe (1, 10-phenanthroline)$_2$(NCS)$_2$]

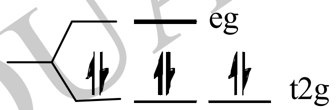


- Since NCS is ambidentate ligand therefore change in co-ordinate mode.
- Change in the spin-state of iron of high temperature.

4.Sol. $k_4[Fe(CN)_6] = [Fe(CN)_6]4^-$

Fe is present in symmetric field

$Fe^{2+} \rightarrow 3d^6 \rightarrow$ low spin complex



As the ligand environment and the electronic environment is spherical in nature. Hence EFG = 0, So, it will show only one line.

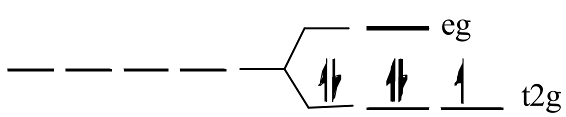
IR : 1760 cm–1

^{1}H NMR : δ(ppm) : 7.2 (1H

5.Sol. $k_3[Fe(CN)_5No] \Rightarrow [Fe(CN)_5NO]3^-$

Fe is present in asymmetric ligand environment

$Fe^{3+} \rightarrow d^5 \rightarrow$ low spin complex



Both, the ligand as well as the electronic enviroment is non-spherical. so, EFG ≠ 0, the complex will exhibit two lines in Mössbauer spectra.

$\therefore$ $k_4[Fe(CN)_6]$ and $k_3[Fe(CN)_5No]$ consist of one and two lines respectively.

6.Sol. The isomer shift value of the complexes are given below :

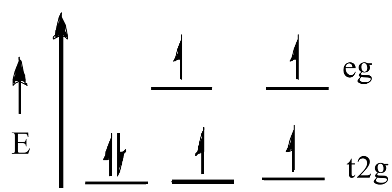
L	**δ(mm/sec)**
NO^+	0
CO	0.15
PPh_3	0.23
NO_2^-	0.26
NH_3	0.26

In ^{57}Fe, ΔR = –ve, so higher the δ–electron density, lower the isomer shift and higher the d-electron density, high the isomer shift.

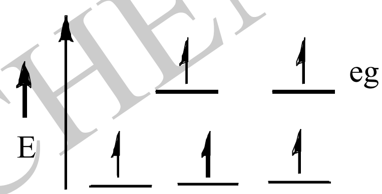
The increasing order of Π-acidity of ligands is $NH_3 < PPh_3 < CO < NO^+$. Higher the Π–acidity of the ligand higher will be the donation from the filled do-orbital of the metal will be less. For Fe, lower the number of d-highest Π–acceptor property, the d-orbital electrons of the metal will be less.

For Fe, lower the number of d-electrons, lower will be the isomer shift. The Increasing order of chemical shift of the low spin complexes of $[Fe(II)\,(CN)_5L]n^-$ with respect to ligand is $NO^+ < CO < PPh_3 < NH_3$

7.Sol. Fe(II) $\rightarrow d^6 \rightarrow$ high spin Fe(II) $\rightarrow d^5 \rightarrow$ high spin



Electronic environment is non-spherical



Electronic environment is spherical

Fe	Fe+	Fe2+	Fe3+
$3d^64s^2$	$3d^64s^1$	$3d^64s°$	$3d^545°$

$Fe^{+2} > Fe^{3+} > F^{e+} > Fe$

(Higherd-electron density) (Highers-electron density)

So, the high sipin complexes of Fe(II) have more isomer shift values than Fe(III) and the isomershift of Fe(II) and fe(III) both are positive.

Fe(II) > Fe (III) both are positive.

8.Sol. Isomeric shift value of SnF_4 is minimum

$SnF_4 = -0.36$

$SnCl_4 = 0.86$

$SnBr_4 = 1.15$

$SnI_4 = 1.55$

In^{119}Sn, ΔR = +ve higher the δ-electron density, higher ther isomer shift and higher the d-electron density lower will be the isomeric shift. In SnF_4, it is an ionic, so, environment of Sn doesn't remain spherial due to its's polymeric structure.

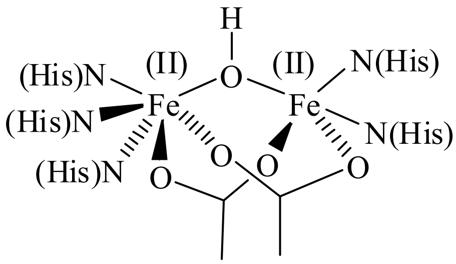
$SnCl_4$, $SnBr_4$, SnI_4 are covalent molecules and have sp^3 hybridisation.

Higher the electronegativity, lower will be the 's' electron density and lower will be the isomer shift value.

9.Sol. Isomer shift depend upon s-electron density around the nucleus.

In Fe complex $\rightarrow$ s-electron density increases isomers shift decreases.

In Sn complex $\rightarrow$ s-electron density increases isomer shift increases.

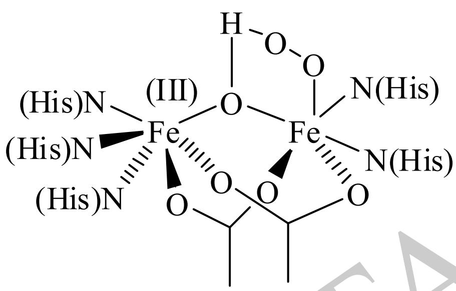
10.Sol. 

Deoxy-hemerythin

Fe(II) : high spind^6

- Weak antiferomagnetic coupling
- So, paramagnetic in nature

So, the number of lines in Mössbauer spectra of deoxy-hemerythin is one doublet and it is pramagnetic in nature.

11.Sol. 

Oxy-hemerythin

Fe(III) : high spin d^5

- Strong anti-ferromagnetic coupling
- So, diamagnetic in nature

The number of lines in Mössbauer spectra of oxy-hemerythin in two doublet and it is diamagnetic in nature.

12.Sol. In Sn complex, isomer shift increases with increasing s electron density.

Valence state	chemical shift (mms–1)
Sn+4 (5s°5p°)	0
Sn	2.1
Sn^{2+} ($5s^2$ 5p°)	3.7

So. the correct relation, Sn^{2+} > Sn(covalent) > Sn^{4+}

13.Sol. In all the complexes the electronic configuration is t2g6 eg° itself symmetric. Here, the asymmetric in electron distribution arises only from the ligand non-equivalence which give C_{4v} symmetry, not only the electron density around the nucleus

14.Sol. In low spin complexes of Fe(II) and Fe(III), the isomer shifts values in both the complexes almost comparable and negative value generally found.

Because the relative efficiency of the metal $\rightarrow$ ligand, Π-bonding in the low spin complexes of Fe(II) and Fe(III)

Note : Sometimes it may be more negative for the Fe(II) complexes.

17 **Sol:** is less but the degree of asymmetry in electron distribution is also less from moving.

$\xrightarrow{NH3: \rightarrow NO^{+}}$

So more Π-acceptor ligand causes as imblance in the electron distribution around the Fe-nucleus. This asymmetric electron distribution around the Fe-nucleus mainly due to heavy electron withdrawal in one direction. [Fe → NO^{+}] produce a higher EFG at the nucleus to cause the higher quadrupole splitting.

$\boxed{NH_3 < PPh_3 < CO < NO^{+}}$